REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
30-12-2011	Performance/Technical Report (Monthly)	12/1/2011 - 12/30/2011

4. TITLE AND SUBTITLE

Polyfibroblast: A Self-Healing and Galvanic Protection Additive

5a. CONTRACT NUMBER

5b. GRANT NUMBER

N00014-09-1-0383

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER

5e. TASK NUMBER

FGY25

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
875 North Randolph Street
Arlington, VA 22203-1995

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release: distribution is Unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

15. SUBJECT TERMS
corrosion protection, self-healing, coatings, polymers

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jason J Benkoski
U	U	U	UU	4	19b. TELEPHONE NUMBER *(Include area code)* 240-228-5140

POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #1

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Reporting Period: December 1 2011 through December 30, 2011
Date of Report: December 30, 2011

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1 Summary

Our initial goal is to solve two major processing hurdles discovered during FY11: shorten the microcapsule polymerization time from several days to several hours, and dry the samples without resorting to freeze-drying. The former has been shortened to overnight, and the latter appears to have been solved by using anti-caking additives during filtration.

2 Project Goals and Objectives

While we await additional funding and the establishment of a subcontract agreement, we will use our first $30k allocation to improve the speed, cost, and scalability of our sample preparation protocol.

3 Key Accomplishments

3.1 Pre-Kickoff Meeting

A formal kickoff meeting including APL, PPG, and ONR will be scheduled as soon as the remaining funding arrives. In the interim, we held an informal kickoff meeting at APL to outline our plan for the first $30k allocation. The first month will focus solely on manufacturability. By developing an improved processing protocol up front, we can benefit from improved sample making efficiency throughout the year. In addition, sample preparation methods will remain static and will not cause unexpected variations in coating performance.

At the meeting we reviewed the formulations that were tested in FY11, identified the most promising samples, and made plans to repeat those experiments. We also outlined a series of new formulations that will be tested in FY12 to further optimize performance. The experiments were then scheduled to align with the milestones outlined in the FY12 technical proposal.

3.2 Drying

If the microcapsules are filtered and dried on the benchtop, they suffer irreversible clumping. To date, we have addressed this problem by freeze-drying. Freeze-drying results in free-flowing powders that mix readily with primer resin to form the Polyfibroblast primer. Unfortunately, freeze-drying is a slow and costly process that does not translate well to mass production.

Previous attempts to improve drying have mostly involved transfer of the microcapsules from water to a solvent with a lower boiling point and/or surface tension. This approach did not completely solve the caking problem, and solvents such as methanol and acetone frequently damaged the microcapsules in the process.

Preliminary experiments indicate that anti-caking agents may allow us to air dry the microcapsules after filtration. So far, sodium dodecylsulfate and Brij 30 surfactant have resulted in free-flowing powders after only one hour of drying on the benchtop.

3.3 Interfacial Polymerization

Another manufacturing issue identified in FY11 was the slow cure time for the polymer skin layer. It currently takes three days to fully form the outer polymer shell of the microcapsules. Most attempts to speed this reaction result in unwanted internal polymerization and through curing. Preliminary experiments have shown that toluene diisocyanate and ethylene diamine may react more quickly at the interface than previously thought. With a functionality of two, these monomers can only form a linear polymer. Our previous experience actually showed that such chemicals were actually *more* prone to internal curing. The difference here may be that the formulation now includes a high volume fraction (75%) of silane coupling agent. Since the silanes do not polymerize, they may help to limit the precipitation of polyurea within the microcapsule interior.

4 Next Steps

4.1 Synthesis Improvements

Further experiments will be performed to verify that surfactants prevent caking and further optimize the process. We will also test to make sure that the surfactant residue does not adversely affect the subsequent primer performance.

We will continue to investigate ways to increase the microcapsule formation for 75% octadecyltrimethoxy silane (OTS) microcapsules. Lessons learned for the 75% OTS microcapsules will then be applied to our more typical formulations.